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Do, Quyet H.; Ngo, Thanh K.V.; Sporken, Robert; PHAM THANH TRUNG, X

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Author: Trung T. Pham Quyet H. Do Thanh K.V. Ngo Robert Sporken

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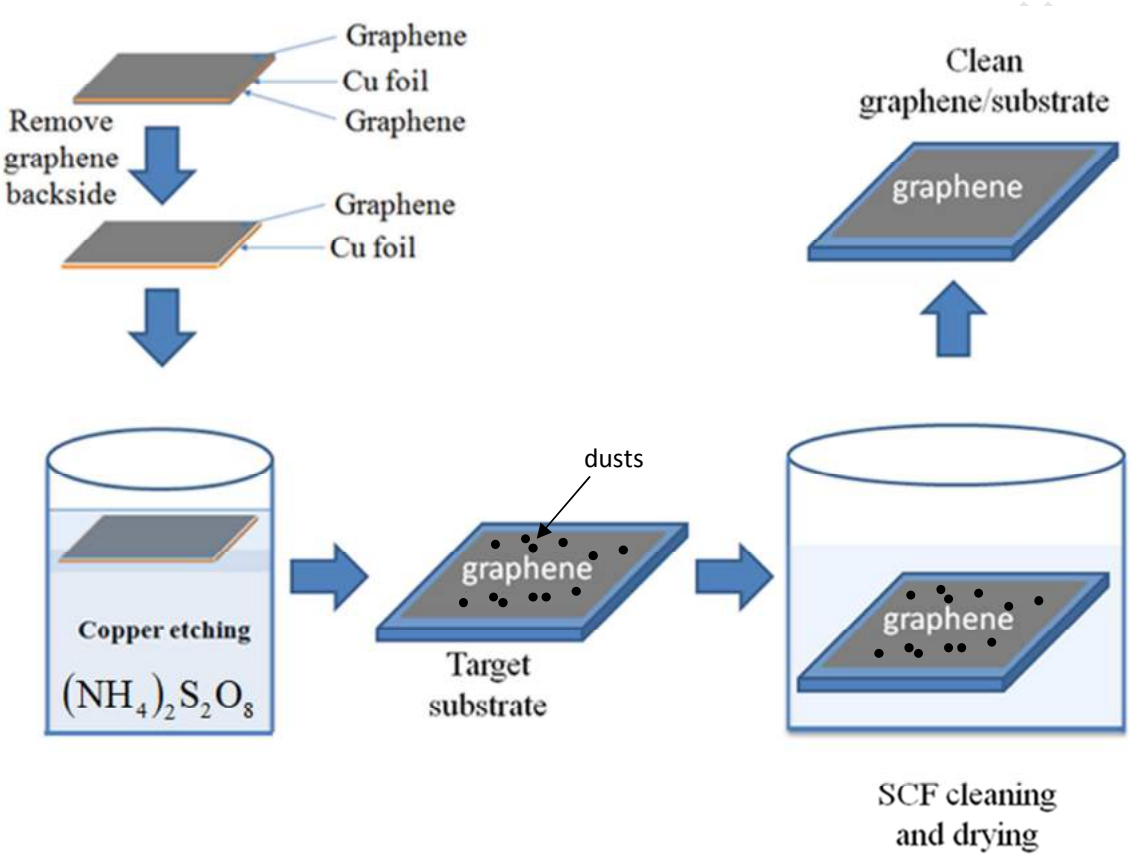
Graphical Abstract



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Direct transfer of the CVD-grown graphene on copper foils on SiO_2 substrate under supercritical CO_2 assisted-cleaning technique

Trung T. Pham,[1, 2, 3, *] Quyet H. Do,[2] Thanh K. V. Ngo,[2] and Robert Sporken[3]

[1] *Department of Materials Technology, HCMC University of Technology and Education, 01 Vo Van Ngan street, Thuduc district, 700000 Hochiminh city, Vietnam*

[2] *Research Laboratories of Saigon Hi-Tech Park, Lot I3, N2 street, District 9, 700000 Hochiminh city, Vietnam*

[3] *Namur Institute of Structured Matter (NISM), Department of Physics, University of Namur, 61 Rue de Bruxelles, B-5000 Namur, Belgium*

The transfer of CVD-grown graphene sheets onto arbitrary substrates is important for the development of practical applications. Unfortunately, designing a low cost and highly efficient graphene transfer technique to achieve defect-free graphene sheets with low contact resistance onto various substrates still remains a challenge. In this paper, a CVD grown monolayer graphene sheet was directly transferred on SiO_2/Si substrate. We found that a combination of floating copper with graphene films on ammonium persulfate solution with an original method of supercritical CO_2 fluid can effectively produce clean and dry samples without damaging the crystalline quality of graphene. This method does not require any polymeric material to be desposited on the graphene films at any stage. Samples are analyzed by optical microscopy, Raman spectroscopy, scanning electron microscopy and atomic force microscopy. This method is very promising for cleaning graphene samples for electronic device fabrication.

I. INTRODUCTION

Nowadays, graphene is known as a unique two-dimensional system with excellent physical and chemical properties that has opened new possibilities not only for fundamental physics research but also for industrial applications [1, 2]. Therefore, enormous efforts during the past fifteen years have been devoted for growing and transferring graphene sheets on various substrates for further applications using different methods such as mechanical exfoliation of highly oriented pyrolytic graphite (HOPG) [1], chemical vapor deposition (CVD) on metal substrate [3], thermal decomposition of SiC in ultra-high vacuum (UHV) [4], etc. Among these techniques, SiC graphitization seems to be the best method to produce large area epitaxial graphene layers directly on the substrate [5]. However, it is hard to achieve high quality graphene sheets from the SiC surface using traditional wet and dry transferring techniques [6]. On the other hand, CVD method has been considered as one of the best way to grow and transfer wafer-scale graphene sheets from metal substrates such as Ni, Ru, Ir, Pt, Co [8–11, 60], and Cu [12, 13], in which copper is the most investigated catalyst because it is inexpensive and widely available; single layer graphene grown on Cu by CVD can be of high crystalline quality. Therefore, there are many publications on the graphene synthesis using various kinds of copper substrates that can be summarized as follows: commercial copper [14, 16–19] or high purity copper foils [17, 18], copper single crystals [19], thin copper films deposited onto thin layers grown on silicon wafers [20–22], copper thin films heteroepitaxially grown on sapphire [23, 24], and melted copper [25, 26], copper nanoparticle hybrids [27], graphene transfer from copper to gold nanoparticle arrays [28], oxygen-passivating active sites of Cu surface for sensor fabrication [29]. In addition, growth conditions of graphene on copper extend from atmospheric

*Corresponding author: trung.phamthanh@shtplabs.org

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[13, 14] and low pressure [16, 17, 19] to ultra-high vacuum [18]. Despite of the huge potential of graphene applications in the field of electronic devices such as high-speed graphene transistors [30], transparent electrodes in solar cells [31], light emitting diodes [32], optoelectronics [33], sensors [34], the development of highly efficient graphene transfer technique to achieve a non-defective graphene sheets with low contact resistance onto various substrates still remains a challenge. The remaining residues and dusts from graphene transferring processes strongly affect the bonding, and contact resistance of the graphene sheets with substrates and can hamper applications. The main disadvantages of the traditional graphene transfer process using a liquid solution to oxidize the copper substrate and a polymer to support the graphene layer are the unintentional contamination of nano-sized materials due to strong interaction between the polymer and the graphene surface as well as the high surface tension of the liquid solution [35–37]. Therefore, direct transfer of graphene films onto target substrates is highly desirable. There have recently been several attempts to transfer graphene directly on SiO_2/Si wafer. For example, Lin et al. [39] presented a polymer-free method for transferring graphene grown by CVD to any substrate via using pumps for injecting solvent and extracting etchant to dilute solution before graphene absorption on the target substrate. Although this is an interesting way to obtain a clean graphene film on the substrate, it is rather complicated and lengthy process. In the same purpose, Zhang et al. [38] reported a new method for transferring CVD-grown monolayer graphene based on the use of a biphasic configuration combining etchant solution of ammonium persulfate and low viscosity liquid organic layer of n-hexane during the copper wet etching. The main advantage comes from using this hexane layer to replace the deposited polymeric materials used in the majority of current graphene transfer methods that can cause severe contamination problems. However, this technique may be appropriate only for transferring a fully covering graphene or multilayer graphene rather than graphene flakes/domains because it is very easy to damage or break the graphene films in the solution or if the substrate is transferred into a new hexane/pure water interface for further cleaning. This is due to the much higher viscosity of water compared to the solution of ammonium persulfate in water at room temperature, resulting in an increase of the surface tension which could be harmful to the transfer of graphene films on a substrate [39, 44]. In addition, n-hexane is a highly volatile aliphatic hydrocarbon which should be avoided in the long process of copper etching [40]. Especially, it is very difficult to completely transfer graphene with relatively small sizes (about a few tens of micrometers) on copper to the target substrate because it is easily broken into many flakes during fishing graphene films in water by a substrate. In order to avoid this problem, in this paper we suggest a simple technique to scoop graphene sheets out from the solution of ammonium persulfate using an arbitrary substrate after complete etching of copper, followed by using a supercritical CO_2 fluid which exhibits superior properties such as no surface tension, high solvation possibility, and high diffusivity in order to remove further contamination from the sample surface [41–43]. We found that a combination of this transferred technique with an original method of supercritical CO_2 fluid can effectively clean and dry the sample surface without damaging the crystalline quality of graphene. This method can be used to transfer any crystal size of graphene from copper to any type of arbitrary substrate. Our experimental results are investigated in detail by optical microscopy (OM), Raman spectroscopy, scanning electron microscopy (SEM) and atomic force microscopy (AFM).

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II. EXPERIMENTAL DETAILS

Mono-/double-layer graphene on copper foils was synthesized using a CN-200TH ULVAC - Japan via a combination of CH_4 and H_2 at a substrate temperatures of 1000°C. By changing the growth conditions such as substrate material, substrate temperature, composition of the reaction mixture, and pressure or flow rate of different gases, various structures and properties of deposited material can be obtained. High purity of the reactive gases, and low deposition rate enable growth of single-/double-layer graphene with high level of coverage and high crystalline quality on copper foils.

A. Graphene growth

Polycrystalline copper (99.99% purity, 25 μm-thick pieces) was purchased from MTI corporation (US) with a coverage of native oxided layers. These substrates were cleaned in acetone in an ultrasonic bath for 15 min, then in isopropanol for 15 min, and finally blown dry with nitrogen. The superficial copper oxide is removed by etching in acetic acid (99.5% purity) at room temperature for 10 min, followed by rinsing in deionized water, then by acetone to remove the remaining impurities on the sample and the copper piece is blown dry with nitrogen. Immediately, the sample is mounted on a sample holder and introduced into the horizontal quartz reactor at room temperature. The synthesis process is summarized by the temperature-time diagram in Fig. 1 (a).

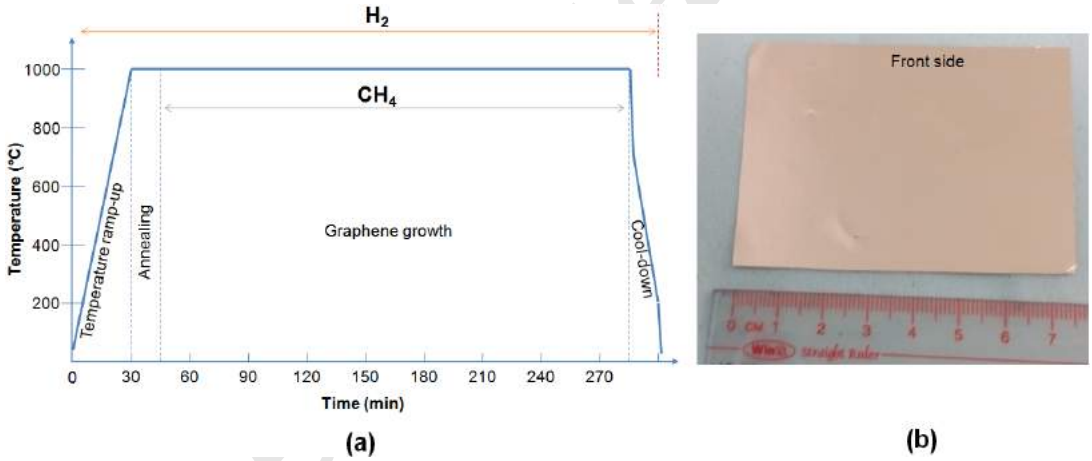

FIG. 1: (a) Temperature profile of a typical 4-stage LPCVD growth process for obtaining graphene on copper foils; (b) an area of copper foil around (7.5×5) cm^2 after mono-/double-layer graphene coverage.

Next, the copper piece is heated slowly up to 1000°C in H_2 (200 sccm, 99.999% purity) environment. When the substrate temperature reaches 1000°C , it is maintained there for 15 min. Mono-/double-layer graphene is then grown by admitting 0.5 sccm of CH_4 (99.99% purity) for 3 hours as detailed by Refs. [45, 46] at pressure $\sim$ 10 Pa. The sample is cooled rapidly (100°C/min) between 1000°C and 700°C, then slowly ($\sim$ 50°C/min) between 700°C and room temperature (RT). The whole process is done under constant flow of 200 sccm H_2. As a result, mono-/double-layer graphene films cover on both sides of an area of $\sim$ (7.5×5) cm^2 copper foils as shown in Fig. 1 (b).

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B. Etching, transferring and cleaning techniques

Graphene/copper/graphene samples were processed by removing the graphene grown on the backside of the copper foil by etching in a solution of 0.1M of $(NH_4)_2S_2O_8$. The advantage of using ammonium persulfate instead of $FeCl_3$ and $Fe(NO_3)_3$ solutions [47, 48] is that it can minimize the resulting nano-sized material residues remaining from the etchant solution. Then, it is eventually floated (graphene side up) on top of this same etching solution, but in another cup in order to etch copper away from the sample. After sufficient etching time ($\sim$ 10 hours), only the synthesized graphene sheet remained on top of the solution surface. The free-standing graphene sheet was scooped out of the solution using a substrate of interest and was left to dry at room temperature. In the present work, SiO_2/Si substrates were used. At this stage, graphene transferred onto SiO_2/Si substrate was checked by OM, SEM, AFM and Raman spectroscopy, followed by CO_2 supercritical fluid (SCF) treatment in order to remove any residual salt particles or other residue from the backside of the graphene layer. For this purpose, we used a critical point cleaner and dryer with advanced auto-pressure and temperature control from SAMDRI-PVT-3D (USA): The graphene layer on SiO_2/Si was placed and carefully fixed in the stainless steel vessel of the SCF system. After closing the vessel, the SCF of carbon dioxide was built up by firstly increasing the temperature to about 50 - 60°C (above the critical temperature of CO_2), then slowly injecting CO_2 gas from CO_2 tank into the vessel until it reached the pressure of about 75 - 80 bar (above the critical pressure of CO_2). The system was kept in these conditions for several hours to clean the graphene sample, then the CO_2 was purged and the system cooled down to take out the sample for further investigation.

C. Characterization

In this work, samples were analyzed by optical microscopy (Olympus), Field Emission Scanning Electron Microscope (FE-SEM, Hitachi S-4800 (Japan)), Raman spectroscopy using a HORIBA JOBIN YVON spectrometer with a laser wavelength of 632 nm and AFM. AFM images were recorded in tapping mode with a dimension edge version from Bruker. The cantilever and tip are typically manufactured as one unit from silicon of about 100 μm for the length of the cantilever and a nominal apex radius of curvature lower than 10 nm with a typical spring constant of around 40 N/m.

III. RESULTS AND DISCUSSION

First examination of copper foils was performed by optical microscopy as shown in Fig. 2 (a). Results show stripes on the surface of copper foils which may be formed during the manufacturing process. In addition, its surface is stained, which may be a result of the coverage of a native oxide layer with a thickness of a few hundreds nanometers [50]. For this reason, samples were etched in acetic acid (CH3COOH) for about 10 min and then washed with de-ionized water, followed by acetone to remove the remaining impurities on the sample. The resulting surface is shown in Fig. 2 (b). One can see that the copper surface is more uniform and brighter than the one before etching, meaning that its surface is quite clean. Following the annealing of samples at 1000°C in H_2 atmostphere, CH_4 is injected for the synthesis of single layer graphene on the surface of the copper catalyst in Fig. 2 (c). The copper seems to be deformed or recrystallized [51] and looks quite rough with an appearance of grain boundary grooves with hills/ripples

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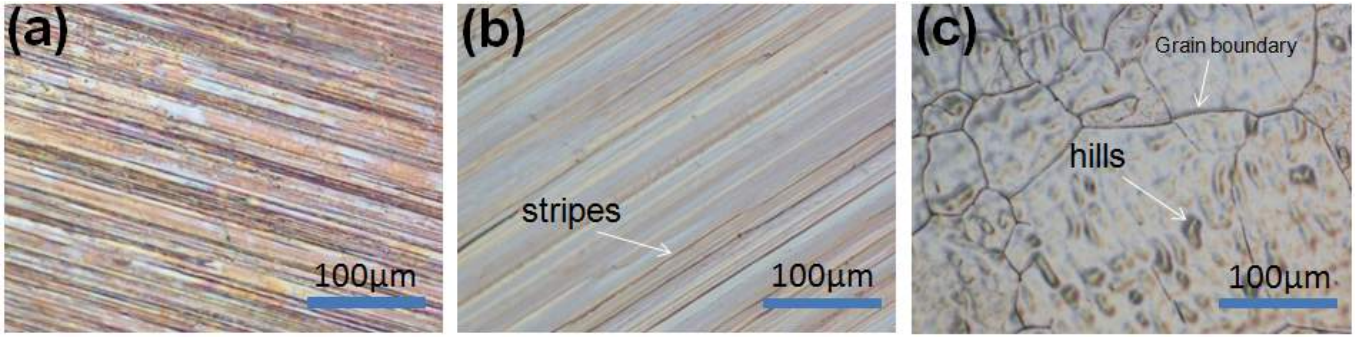

FIG. 2: (a) Bare copper as received from commercial vendors; (b) bare copper after etching; (c) copper surface appears grain boundary grooves, hills and valleys after mono-/ double-layer graphene formation at given conditions.

on the surface, showing a uniform contrast with respect to pure copper (after etching). It is probably a result of copper annealing at 1000°C and fast cooling down to RT.

Fig. 3 shows SEM images obtained on these samples. Surface topography of copper foils (not treated yet in Fig. 3

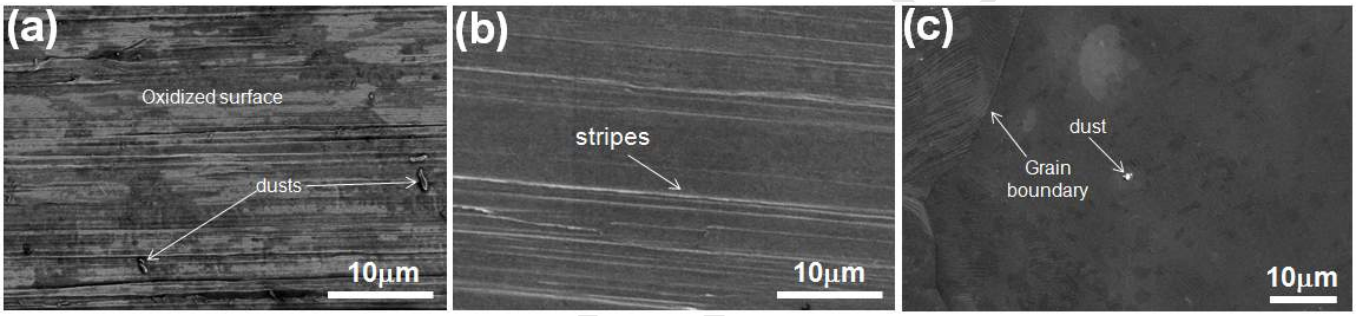

FIG. 3: SEM images of copper surface: (a) copper covered with native oxide layers, (b) copper after etching; and (c) copper after graphene formation at a substrate temperature of 1000°C.

(a)) presents a distinct contrast between surrounding areas with stripes, similar to the images obtained by optical microscopy. Some micron-size particles are also observed. After etching, the surface is clean and uniform with clear stripes which are derived from the nature of copper foils (Fig. 3 (b)). It is consistent with the optical image taken on the same sample (see Fig. 2 (b)). Fig. 3 (c) shows the surface of copper foil after graphene synthesis. Based on the image contrast and gray scale uniformity of its electron reflection, we conclude that the copper surface is fully covered by mono-/ double-layer graphene layers.

The surface morphology as well as the film purity of copper samples before and after graphene formation are further confirmed by AFM images as presented in Fig. 4.

Obviously, surface morphology is completely different after graphene growth on copper as seen in Fig. 4 (c). Compared to bare copper (Fig. 4 (a) & (b)), the surface presents a structure of hills and valleys, but the graphene covered surface is much more uniform than bare copper, as seen in both the topography and the phase image. It indicates that physico-chemical properties of deposited materials do not change much across the sample surface. In other words, copper is covered by a homogeneous film of continuous graphene on top of the sample surface. This agrees with OM and SEM analyses.

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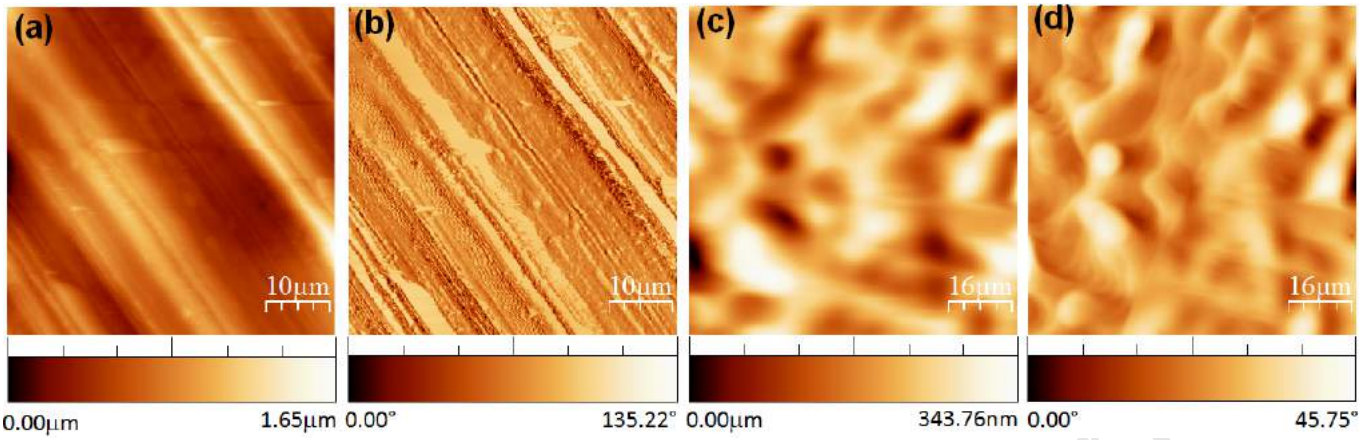

FIG. 4: (a) Tapping mode AFM surface topography of the bare copper and (b) its phase AFM image reflects the difference in contrast between the copper and the oxide impurity on the surface; (c) Tapping mode AFM surface topography of the sample after the LPCVD-grown graphene on copper and (d) its corresponding phase AFM image.

Fig. 5 (a) shows a picture of graphene-covered copper shortly after placing it into a solution of ammonium persulfate ($(NH_4)_2S_2O_8$). Fig. 5 (b) shows the graphene sample after 2 hours in the solution, where it is clear that copper is being dissolved. After 5 hours in the same etchant solution, copper has been fully removed and graphene is now floating on top the solution (Fig. 5 (c)).

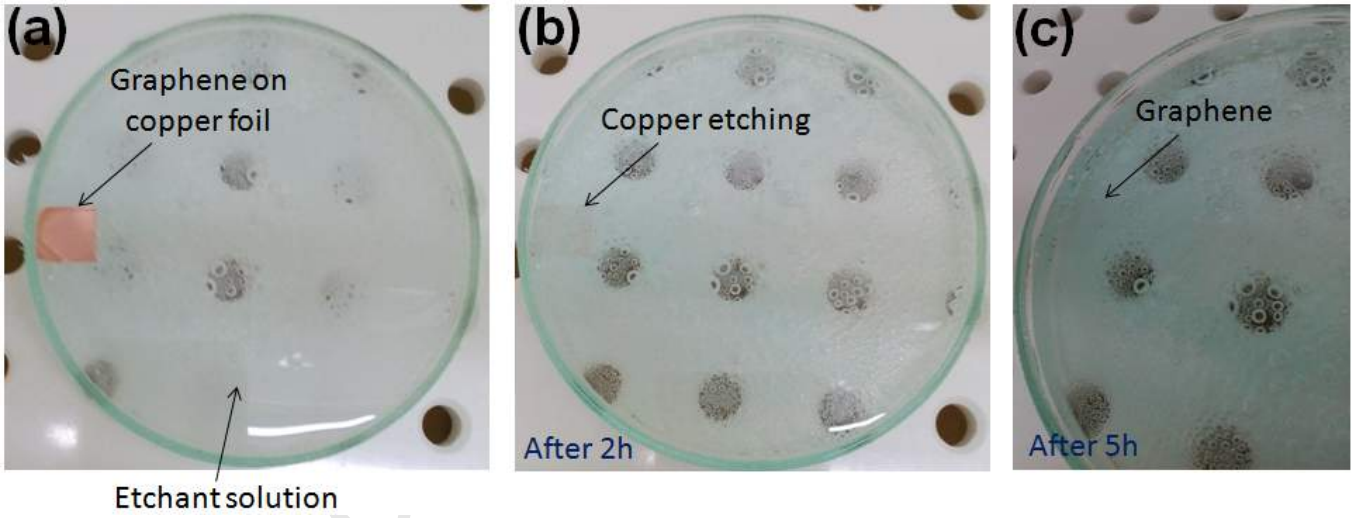

FIG. 5: (a) Graphene/copper foils (1×1 cm^2) in the solution of $(NH_4)_2S_2O_8$; (b) After 2 hours etching; (c) After 5 hours etching in the etchant solution.

Following the copper etching, graphene was directly transferred on a pure SiO_2/Si substrate (Fig. 6 (a)) with graphene sheets spreading out on the surface as shown in Fig. 6 (b). Optically, graphene films on SiO_2/Si substrate is contaminated by residues or salt particles from etchant solution (marked by white arrows). Therefore, it needs to be washed by using a fluid with lower surface tension than common solvents such as acetone, water or a mixture of both. We used a SCF of carbon dioxide, which has been shown to have superioor properties as a cleaning agent [41–43]. After 2 hours of CO_2 SCF (see Fig. 6 (c)), graphene was found to be remarkably clean compared to the situation

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before SCF treatment. However, graphene films seem to be folded and/or broken which is probably induced during the cleaning process.

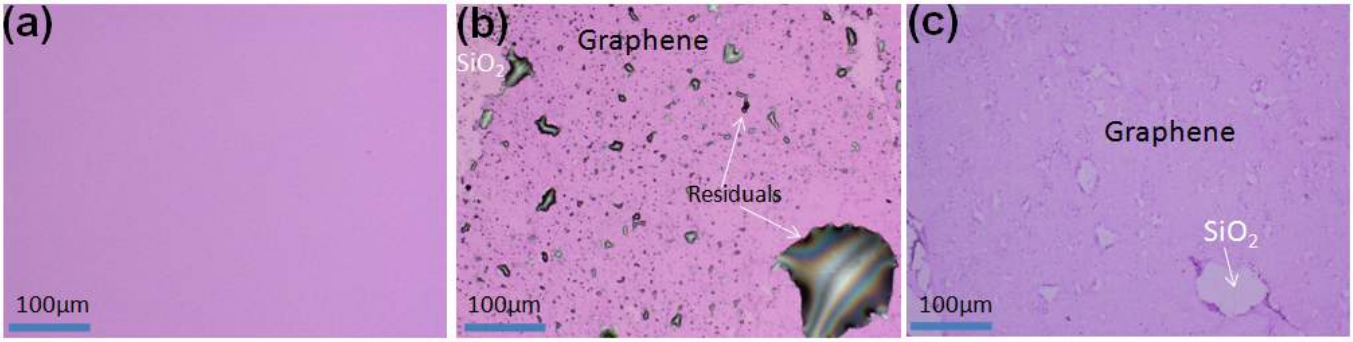

FIG. 6: (a) Pure SiO_2/Si substrate; (b) Direct transfer of graphene sheets onto SiO_2/Si from the solution of ammonium persulfate; (c) After cleaning by using SCF of carbon dioxide during 2 hours.

In order to evaluate the role of CO_2 SCF in cleaning graphene samples, SEM measurements were performed in Fig. 7. Some images were taken with low magnification before and after CO_2 SCF as shown in Figs. 7 (a) & (c), respectively. Untreated graphene samples are heavily contaminated (see Figs. 7 (a) & (b)) which obviously comes from a precipitation of the etching solution after drying at room temperature. Most of the residue is removed by CO_2 SCF in Figs. 7 (c) & (d). Although graphene films seems to be folded, wrinkled (marked by white arrows), graphene flakes are similar to the original ones on copper (some double layers still maintain).

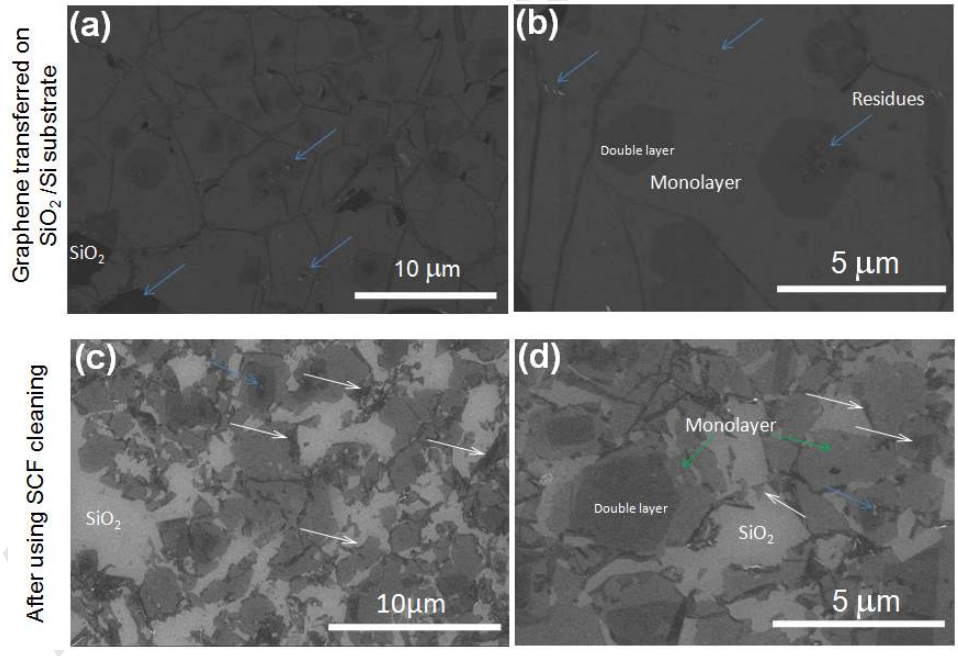

FIG. 7: SEM images were taken after (a) & (b) direct transfer onto SiO_2/Si substrate with the presence of much residue and many salt particles (marked by blue arrows); (c) & (d) after using the SCF of carbon dioxide with folded or overlaps or broken as marked by white arrows. Green arrows mark mono-layer graphene flakes.

For more details, AFM images were recorded on all samples (Fig. 8). Again, much dust and residue is observed after direct transfer from the etching solution onto SiO_2/Si substrate, in both the topography image (Fig. 8 (a)) and

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the phase image (Fig. 8 (b)). Samples appear more uniform after SCF of carbon dioxide treatment. As expected, all residue was removed from graphene sheets (see Fig. 8 (c)), but folds or wrinkles appear on the surface (marked by green arrows) and the SiO_2/Si substrate is uncovered in some areas (marked by white arrows). The AFM phase image exhibits only weak contrast differences (Fig. 8 (d)), indicating uniform physico-chemical properties of transferred graphene films. In other words, samples are clean with a coverage of mono-/double-layer graphene on top of the surface. The cleaning effect of SCF CO_2 after wet etching has been reported for semiconductor device fabrication [52]. It seems that the SCF state of CO_2 is important to explain the cleaning properties. Indeed, in the gas phase, the fluid can easily flow in and out of any hole, edge etc. within the sample and carry away tiny particles that are stuck there. Because of its high density, the fluid also has liquid properties with a strong solvation power that can dissolve many substances, including residue from the etching solution. During the CO_2 venting, most of the dust and residue follows the CO_2 flow out of the chamber. This doesn't happen in the normal drying process as the solid will remain or deposit on graphene after the solvent is dried out.

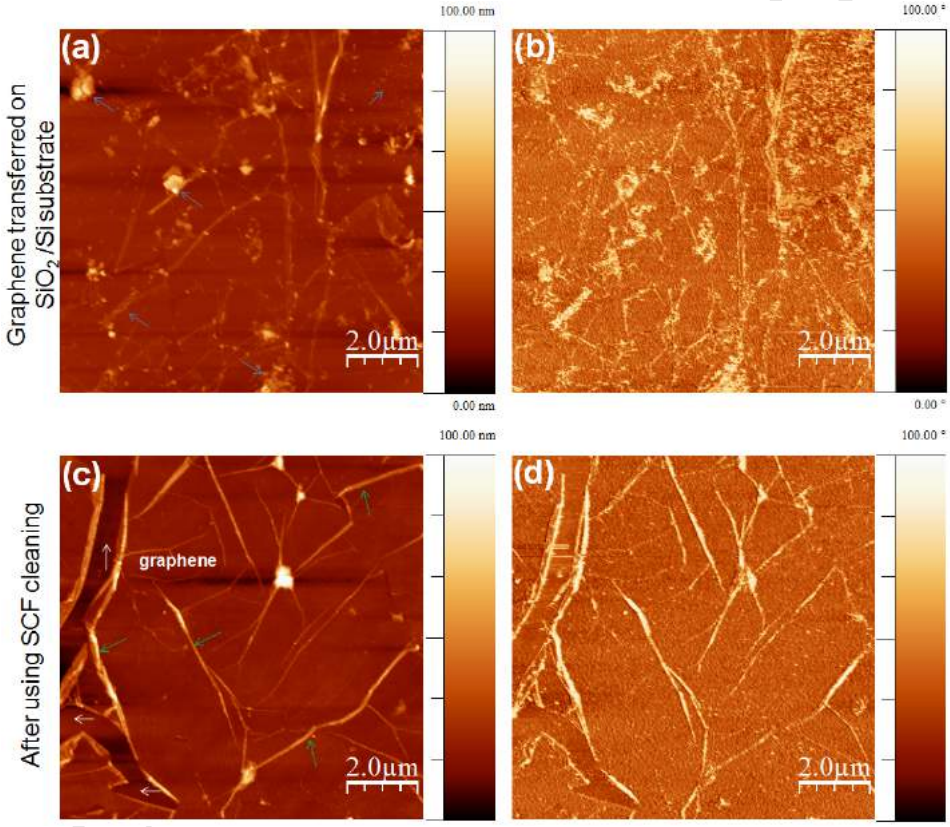

FIG. 8: (a) Tapping mode AFM surface morphology of the transferred graphene on SiO_2/Si substrate with dusts/residues on the surface (marked by blue arrows) and (b) its corresponding phase AFM image; (c) The same graphene sample after using the SCF of carbon dioxide to wash the graphene surface with an appearance of wrinkles/overlaps (marked by green arrows) and (d) its corresponding phase AFM image.

To investigate the crystalline quality of our graphene samples, Raman measurements were carried out using a 632 nm (1.96 eV) laser. The results are shown in Fig. 9.

The most important peaks in the Raman spectrum are the D, G and 2D peaks which occur at approximately 1350 cm^{-1}, 1580 cm^{-1} and 2700 cm^{-1}, respectively. The spectrum has large, symmetrical G and 2D peaks indicating the

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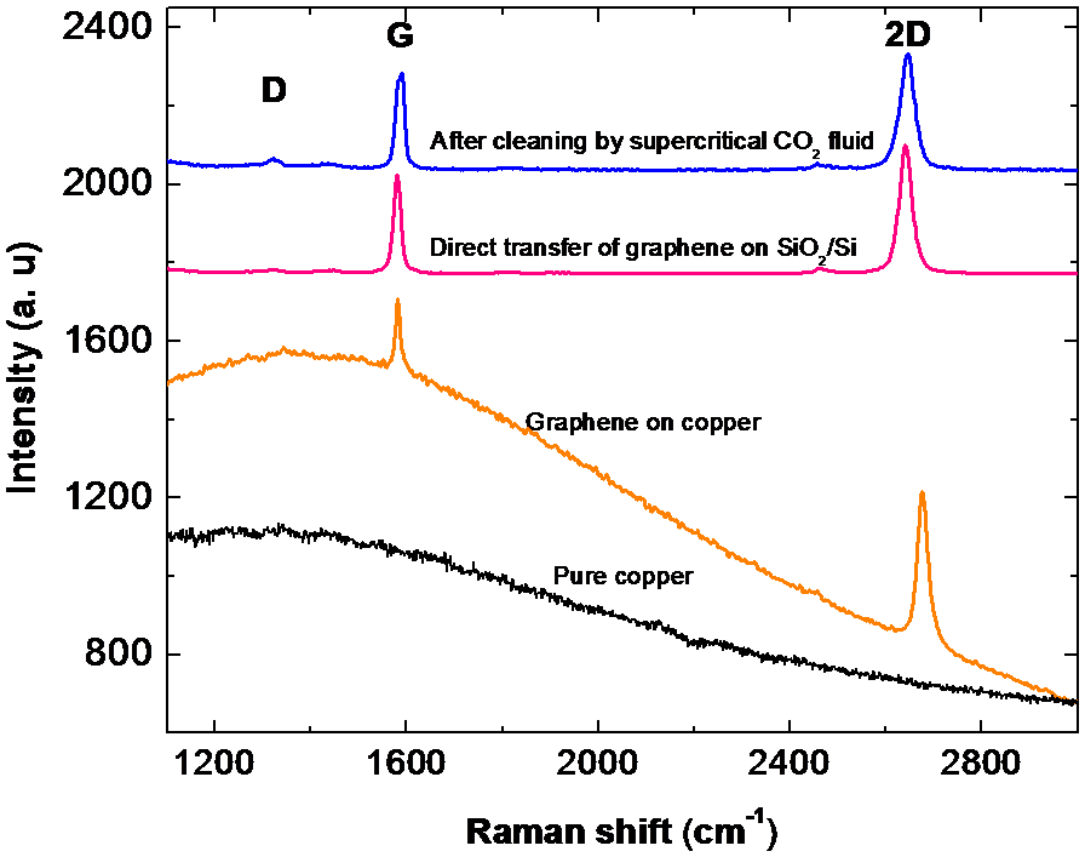

FIG. 9: Raman spectra of studied samples before and after graphene formation on copper, followed by direct transfer on SiO_2/Si and using the SCF of CO_2.

presence of graphene layers in which the I_{2D}/I_G peaks ratio is larger than 2 which is for mono-/ double-layer graphene [57]. For graphene systhesis on copper, one can see that the G and 2D peaks of graphene on copper are very intense with the high background intensity due to elastic scattering and the fluorescence effects of copper [58, 59], confirming the high crystalline quality of graphene formation on copper foil. Also, the very small D peak suggests that defects are minimal. For transferred graphene on SiO_2/Si substrate, the D peak intensity was found to be small in the given area which indicates good quality transfer. However, the FWHM of 2D peak (~ 33 cm^{-1}) is larger and its integrated intensity ($I_{w/}$) is also little bit higher than the one before SCF (~ 27 cm^{-1}, $I_{w/}/I_{w/o} \sim 1.03$). It may be explained by the fact that graphene films are now folded and wrinkled or overlapped after SCF process as confirmed by AFM images. Raman signal recorded on graphene sample after cleaning and drying by SCF of CO_2 presents a small D peak, meaning that the crystalline quality of graphene films remains good after cleaning. It strongly supports our conclusions on the potential of this technique for cleaning graphene surface.

From the above characterization, we must point out that a clean sample of transferred graphene was obtained via a combination of floating copper with CVD-grown graphene films on an ammonium persulfate solution with the SCF carbon dioxide treatment. Although graphene films seem to be folded/wrinkled or broken after cleaning, it is shown that the SCF of carbon dioxide significantly improves cleaning of the tranferred graphene on SiO_2/Si substrate. This is very promissing for cleaning graphene samples for electronic device fabrication.

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IV. CONCLUSIONS

Direct transfer of graphene onto SiO_2/Si substrates using the SCF of carbon dioxide as a cleaning agent has been demonstrated. For the transfer of graphene sheets onto target substrates, we found this new technique to be extremely effective compared to conventional ones which use liquid solutions exhibiting high surface tension. The use of the SCF technique required no polymer supports, which are major contamination sources for graphene surfaces. Although graphene films seem to be folded or broken after cleaning process, the importance role of SCF properties to remove undesired contamination is demonstrated. From these promising results, it would be valuable to further evaluate this SCF cleaning technique to produce a less defective and cleaner graphene surface for the manufacturing of powerful graphene based electrical devices. In the future, we will investigate further details regarding effects of various supercritical fluids including water, acetone, carbon dioxide as well as their mixtures, which possess much higher solvation power than carbon dioxide.

V. ACKNOWLEDGMENTS

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